THE DIELECTRIC BEHAVIOR OF SOME POLAR SUBSTANCES IN THE REGION OF PHASE TRANSFORMATION

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In this article we report the results of measurements of dielectric constants of some polar substances over a wide temperature range with a specific reference to the phase transformation. Substances which we investigated are: 1,2 dichloretane, chlorobenzene, benzyl alcohol and benzaldehyde. The experiments were made in the temperature range from 40 °C to —180 °C and included beside the liquid also the solid state of this substances.

The experimental method

The dielectric constant was investigated by measuring the capacity of a condenser, platinum plates of which were in direct contact with the examined substances. The capacity of the condenser in the air was about 1.5 pF. The measuring cells were made of Pyrex-glass, locked up with a teflon stopper, which served as the carrier of the condenser. The volume of the measuring cell was about 2 cm^3.

We calibrated the measuring condenser at 20 °C with substances as recommended in the references [1—3]. At the determination of dielectric constants we applied the method of contact-measuring condenser [2, 4]. The temperature was measured with a copper-constantan thermocouple.

Corrections for the effects of thermo-deformation and other parameters were applied at the final form of the results. These corrections were based on the performance of the measuring cell, with air as dielectric medium, in the temperature interval in which the measurements were performed.

The capacity and the conductivity were determined with the aid of an impedance bridge, Wayne—Kerr B 331 Mk II Autobalance Precision Bridge, at the frequency 1591.55 Hz ($\omega = 10^4$ Rads/s). Capacity measurements could be done from 100 aF to 1 F and from 10 kS to 1 pS in seven ranges. This equipment made possible the elimination of parasitic capacity and resistance resulting in high reproductibility and precision.

Under −80 °C we used the "Materialprüfkammer" type VMT II from Vötsch. In order to decrease the temperature oscillations and the temperature gradient in the measuring cell, we put it in a copper thermostat which weighted about 1 kg (Fig. 1). The thermal oscillations were in this cell under 0.2 °C.

We determined the temperature dependence of the density of the substances down to the freezing point and its change at the transition into solid state. Volume

changes were measured in a narrow quartz tube of 40 cm length by an optical length meter with a discrimination of 10^{-3} mm.

The substances were of p.a. quality, or puriss. Before application they were purified with a molecular sieve FLUKA AG "Molekularsieb 3Å" and by vacuum fraction distillation. For measurements we always used the middle fraction. The physical constants applied were taken from references [5, 6].

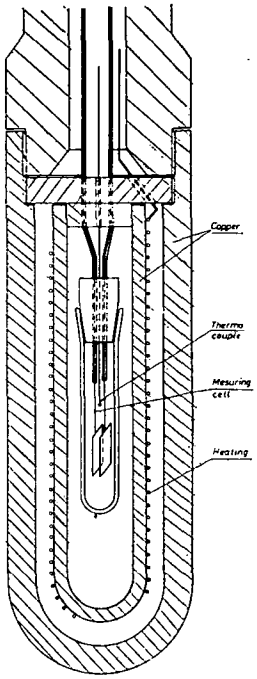

Fig. 1. The measuring cell

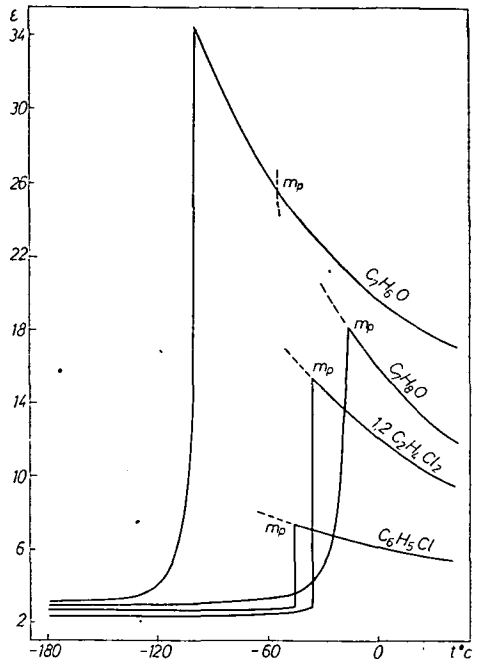

Fig. 2. The variation of the dielectric constant with temperature t

Results

The analitical expressions for the dielectric constant versus temperature in certain temperature range were obtained from the experimental data by the least square method. These expressions were used by the determination of dielectric constants at the temperatures which are given on Fig. 2. and diagrammatically illustrated on Table I. standard deviation of the results in the liquid phase was less than 0.1%, while in solid state about 0.8%. The higher dispersion in solid state was due to thermal deformation of the measuring cell. The analitical expressions for the dielectric constant and the density in liquids, as well as the volume change at freezing are, as follows:

Table I

Dielectric constants as a function of temperature.

t °C	ε				t °C	ε			
	1,2 dichlor-etane	Chlorbenzene	Benzylalcohol	Benzaldehyde		1,2 di-chloretane	Chlor-benzene	Benzyl-alcohol	Benzaldehyde
40.0	9.559	5.338	12.01	17.13	—45.3	—	2.80	—	—
30.0	10.091	5.512	12.83	17.67	—50.0	2.49	2.75	3.41	24.83
20.0	10.671	5.693	13.73	18.25	—55.6	—	—	—	25.64
10.0	11.308	5.886	14.74	18.80	—60.0	2.46	2.72	3.27	26.32
0.0	12.014	6.093	15.87	19.60	—80.0	2.44	2.69	3.16	29.89
—10.0	12.799	6.317	17.15	20.04	—100.0	2.42	2.68	3.07	34.34
—15.3	—	—	17.90	—	—101.3	—	—	—	34.67
—20.0	13.674	6.562	11.90	21.31	—120.0	2.40	2.67	3.01	4.08
—30.0	14.649	6.831	4.92	22.34	—131.0	2.39	—	—	—
—35.9	15.276	—	—	—	—131.0	2.36	—	—	—
—35.9	2.74	—	—	—	—140.0	2.34	2.67	2.97	3.30
—40.0	2.59	7.127	3.76	23.50	—160.0	2.33	2.67	2.95	3.18
—45.3	—	7.296	—	—	—180.0	2.33	2.67	2.94	3.13

a) *1,2 Dichloretane* (1,2 $C_2H_4Cl_2$)

$$\varepsilon = 12.014 - 7.438 \cdot 10^2 t + 3.956 \cdot 10^{-4} t^2 - 1.760 \cdot 10^{-6} t^3,$$

$$V/V_0 = 1.0000 + 1.124 \cdot 10^{-3} t + 1.11 \cdot 10^{-6} t^2,$$

$$-40\,°C\, t \leqq 40\,°C; \quad \Delta V/V_t = -1.84\%.$$

b) *Chlorobenzene* (C_6H_5Cl)

$$\varepsilon = 6.0929 - 2.151 \cdot 10^{-2} t + 8.739 \cdot 10^{-4} t^2 - 5.332 \cdot 10^{-7} t^3,$$

$$V/V_0 = 1.0000 + 9.56 \cdot 10^{-4} t + 1.92 \cdot 10^{-6} t^2$$

$$-50\,°C = t \leqq 40\,°C; \quad \Delta V/V_t = 2.44\%.$$

c) *Benzyl alcohol* (C_7H_8O)

$$\varepsilon = 15.87 - 1.202 \cdot 10^{-1} t + 7.407 \cdot 10^{-4} t^2 - 3.704 \cdot 10^{-6} t^3,$$

$$V/V_0 = 1.0000 + 7.36 \cdot 10^{-4} t + 8.60 \cdot 10^{-7} t^2,$$

$$-30\,°C \leqq t \leqq 40\,°C; \quad \Delta V/V_t = -3.73\%.$$

d) *Benzaldehyde* (C_7H_6O)

$$\varepsilon = 19.60 - 7.527 \cdot 10^{-2} t + 4.482 \cdot 10^{-4} t^2 - 2.736 \cdot 10^{-6} t^3,$$

$$V/V_0 = 1.0000 + 7.82 \cdot 10^{-4} t + 1.50 \cdot 10^{-6} t^2,$$

$$-70\,°C \leqq t \leqq 40\,°C,$$

where V is the difference of the volume in liquid and solid state, and V_0 is the volume of the liquid phase at the freezing point.

Discussion

The dielectric behavior is closely related to the rotation of dipoles, therefore the registration of changes may give us important information about the structure of liquids as well as solids [7—10]. As seen in Fig. 2 the dielectric constant in the substances increased with decreasing temperature down to the freezing point. This behavior may be explained by the effect of temperature on the orientation of dipoles, the molecular interaction, and the change of density. According to the Kirkwood—Fröhlich theory [11, 12] of polarization of polar dielectrics, the dielectric constant is given by the expression

$$\varepsilon - \varepsilon_\infty = \frac{3\varepsilon}{2\varepsilon + \varepsilon_\infty} \cdot \frac{4\pi \varrho N}{3MkT} \cdot \left(\frac{\varepsilon_\infty + 2}{\varepsilon}\right)^2 \mu^2 \cdot g \qquad (1)$$

so that the effect of density and temperature on the orientation of dipoles is given directly; while the effect of temperature on the molecular interaction is given by the correlation factor g. It originates from the interaction of polar molecules with their surroundings. The forces of interaction differ according to their origin and intensity, although they are mainly forces of short range. These result in different types

of associations which contribute to the actual increase or decrease of the dipole moment. g may be calculated theoretically from the expression

$$g = 1 + Z \cdot \overline{\cos \gamma} \qquad (2)$$

where Z is the number of molecules in the direct surrounding of a given dipole, $\overline{\cos \gamma}$ is the average value of the cos angle between adjacent dipoles [11]. The determination of g through Eq. (2) is uncertain, therefore, it will be rather determined from the experimental data applying Eq. (1). For calculations we used $\varepsilon_\infty \sim n^2$, which means a certain approximation. The results of our calculations are given in Fig. 3.

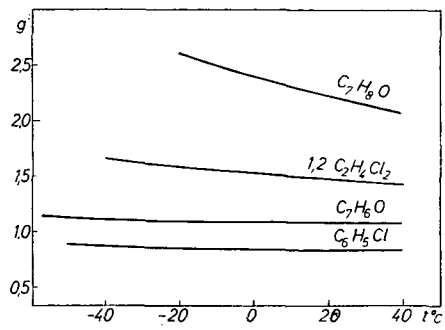

Fig. 3. Correlation factor g as a function of temperature t

a) *1,2 Dichloretane*: A relatively small value and a little increase in the correlation factor with decreasing temperature indicates an association which does not affect significantly the dielectric constant, and shows a tendency towards the parallel orientation of the dipoles. After freezing, the dielectric constant abruptly drops to a small value which decreases very slowly to −131 °C. From these data we conclude that 1,2 dichloretan in solid state may exhibit a small probability of orientational polarization which completely disappears at the above mentioned temperature. The change of dielectric constant beyond this temperature is the result of changes in density.

b) *Chlorobenzene*: The correlation factor is smaller than 1, which shows an association towards the antiparallel orientation and practically doesn't change. The dielectric constant in solid state changes only as a result of changes in density, which means that there is no orientational polarization.

c) *Benzyl alcohol*: The value of the correlation factor is relatvely high and it increases with decreasing temperature which is probably due to formation of association of parallelly oriented dipoles. They are bound by a hydrogen bridge, which is broken at higher temperature. The dielectric constant decreases gradually in solid state and only under −160 °C becomes proportional to the change in density. This may be explained by the existence of orientational polarization even after freezing which is probably due to the alcohol group.

d) *Benzaldehyde*: The change is the dielectric constant is mainly due to the effect of temperature on the orientation of dipoles and changes density, since the correlation factor does not change. At the freezing of the liquid, the orientational polarization does not cease and at about −101 °C the dielectric constant drops abruptly, which is the result of the partial freezing of the dipoles. The orientational polarization does not disappear even at −180 °C and probably originates from the aldehyde group.

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ДИЕЛЕКТРИЧЕСКИЕ СВОЙСТВА НЕКОТОРЫХ СОЕДИНЕНИЙ В ОБЛАСТИ ФАЗОВЫХ ПРЕВРАЩЕНИЙ

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В данной работе сообщаются результаты измерений диэлектрической константы некоторых полярных соединений в широкой температурной области, имея в виду перемену исследованных веществ. Исследованные соединения: 1,2 дихлорэтан, хлорбензол, бензиловый спирт и бензальдегид. Наши исследования мы проводили в температурном интервале от 40 °C до 180 °C, который охватывает как жидкое, так и твёрдое состояния этих соединений.